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Formation of siliceous sediments in brandy after diatomite filtration

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ABSTRACT

Brandy is quite a stable spirit but sometimes light sediment appears. This sediment was separated and analysed by IR and SEM-EDX. It was revealed that the sediment is composed mostly of silica and residual organic matter. Silica was present as an amorphous phase and as microparticles. In an attempt to reproduce the formation of the sediment, a diatomite extract was prepared with an ethanol/water mixture (36% vol.) and a calcined diatomite similar to that used in brandy filtration. This extract was added to unfiltered brandy in different amounts. After 1 month, the Si concentration decreased in all samples and sediments with similar compositions and features to those found in the unstable brandy appeared. The amounts of sediment obtained were directly related to the decrease in Si concentration in solution. Consequently, it can be concluded that siliceous sediment in brandy originates from Si released during diatomite filtration.

1. Introduction

Brandy is a spirit that is produced from wine distillate aged for at least 6 months in oak barrels (European-Union, 2008; Ministry of the Presidency & Spain, 2014). Moreover, Brandy de Jerez is a protected geographical indication produced in Southern Spain (Junta-de-Andalucia, 2005; Schwarz, Rodriguez, Guillen, & García, 2011). Although spirits are quite stable beverages due to the dissolving effect of their high ethanol content, some sediments can be produced by high concentrations of metal ions such as Ca or Mg or by colloidal structured tannins extracted from the barrels (Warwicker, 1960, 1963). Furthermore, sediments with a colloidal structure in brandy de Jerez have been described (Gómez-Benítez, 1992). The silicon contents of alcoholic beverages have been widely determined and in wines the levels vary between 7 and 23 mg/L but they are much lower in spirits (average 1.3 mg/L) (Bauer, Hinkel, Neeb, Eichler, & Eschnauer, 1995; Interesse, Lamparelli, & Alloggio, 1984; Powell et al., 2005). Gómez, Gil, De la Rosa-Fox, and Alguacil (2014) determined silicon contents in brandy de Jerez of around 200 μg/L and found that diatomite filtration releases Si, which can increase in concentration by more than 50% during diatomite filtration. Consequently, the aim of the work described here was to verify whether there is a relationship between the silica released during diatomite filtration and the formation of the observed sediment.

Silica chemistry in alcoholic beverages is complex and is not well understood. In aqueous solution, silica shows the following equilibria (Hamrouni & Dhahbi, 1999; Martin, 2007):

$$SiO_2 + 2H_2O \rightleftharpoons H_4SiO_4$$

$$H_4SiO_4 + H_2O \rightleftharpoons H_3SiO_4^- + H_3O^+$$

$$H_3SiO_4^- + H_2O \rightleftharpoons H_2SiO_4^{2-} + H_3O^+$$

Silicic acid, which is also called monosilicic or orthosilicic acid, is a weak diprotic acid ($pK_1 = 9.6$, $pK_2 = 12.65$) that is almost totally undissociated in natural waters at a pH below 8. However, silicic acid has a precarious general stability and can undergo a succession of dehydration polymerisations. Silicic acid can remain stable as a monomer at concentrations below 100 mg/L, but at higher concentrations it can condense to form insoluble particles and colloids. This is a reversible reaction and depolymerisation by hydrolysis can occur to give the monomer H_4SiO_4 once again. In this way, and depending on the pH, composition and temperature, the amounts of soluble and insoluble silica can vary. Insoluble silica is formed by highly polymerised molecules that form spherical particles with sizes in the range 1–100 nm. In general, these colloidal particles are stable in alkaline solution but in neutral or acidic solutions they can combine to give a gel and sedimentation. It has

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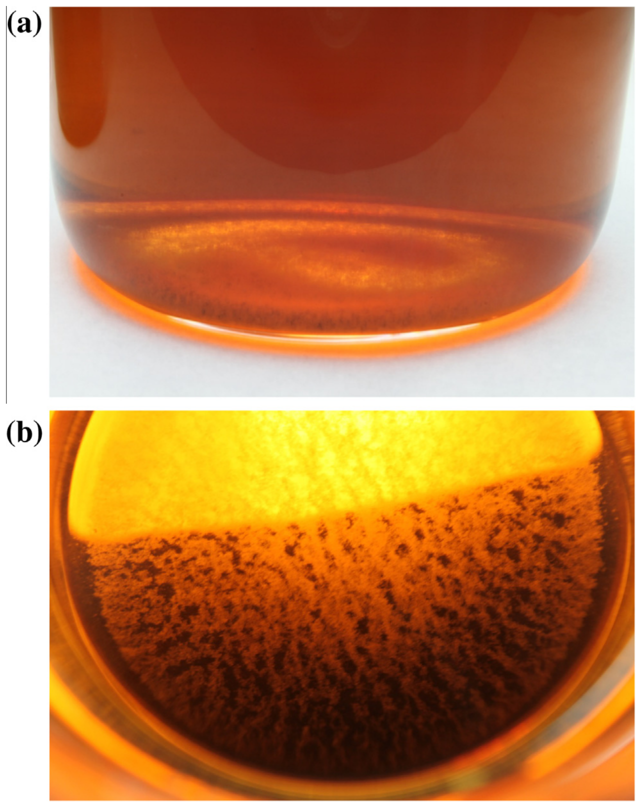

Image 1. Appearance of sediment in brandy. (a) Side view of the sediment in the bottom of the bottle. (b) Top view of the sediment with the bottom of the bottle (half shaded for the sake of clarity).

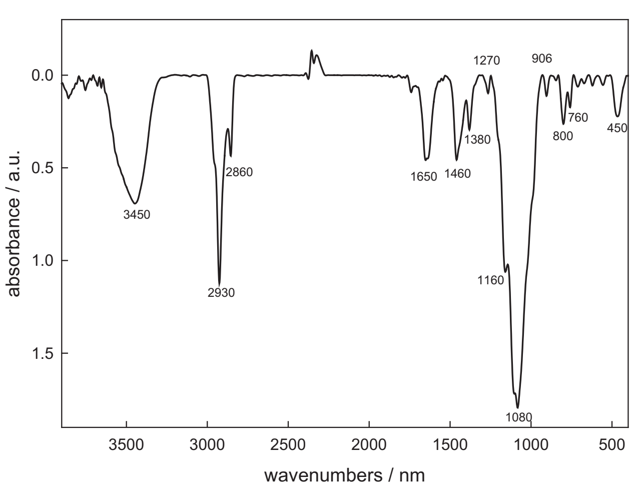

Fig. 1. IR spectrum of brandy sediment.

been found that at pH 7–10 and in the absence of salts, spherical colloids grow without forming particles. However, in acidic solutions or at pH 7–10 in presence of salts, these particles join together to form silica gels. Under certain circumstances these colloids can combine silica with other elements such as Fe or Al and some organic compounds to give amorphous structures (Iler, 1979).

Diatomite filtration is widely employed in the beverage industry. This technique involves the use of a layer of diatomaceous earth placed on a filter element located in pressure vessels. Diatomite filtration employs filter aids in a two-step operation. Firstly, a thin layer of filter aid (called precoat) is built up on the filter holder by recirculating a filter aid slurry prepared with the beverage to be filtered. After precoating, filtration begins and, to prevent clogging of the filter, small amounts of filter aid are regularly dosed to the liquid to be filtered. The filter aid and the suspended particles from the unfiltered liquid are retained on the precoat, which grows continually during filtration, and the tiny filter aid particles create countless microscopic channels that entrap suspended impurities and allow clear liquid to pass through (Sulpizio, 1999; Wang, 2006). Common total diatomite doses used in brandy filtration are 0.4–0.6 g/L. Manufacturers of filter aids produce filter aid grades that cover a wide range of particle sizes to meet practically any industrial filtration requirement. Diatomites used in filtration generally contain >85% silica. Theune and Bellet (1988) defined maximum levels for several chemical constituents of diatomite: CaO < 1% to prevent formation of calcium oxalate and tartrate in beer and wine and Fe_2O_3 < 1.5% and soluble salts <500 ppm to avoid undesirable effects on the composition of the filtered beverage. In addition, OIV. (2002) established parameters for diatomite use in the wine industry, with a maximum drying loss of 1%, a maximum calcination loss at 550 °C of 3%, a maximum soluble products in diluted acids of 2%, a maximum content of iron of 300 mg/kg, lead 5 mg/kg and mercury 1 mg/kg. Diatomite can also contain small amounts of alumina, iron, alkaline earth metals and alkali metals (Mohamedbakr & Burkitbaev, 2009) and even heavy metals such as lead (Stockley et al., 2003) and chromium (Bergner & Braun, 1984) depending on its geographical origin.

The aim of the work described here was to study the composition, structure and origin of the sediment found in brandy.

2. Materials and methods

2.1. Brandy samples

Sediment was separated from commercial Brandy de Jerez (36% vol.) supplied by brandy producers in the Jerez production zone (Southern Spain) in January 2012.

2.2. Separation of the sediment from the unstable brandy

The sediment was separated from the brandy in the bottle by slowly syphoning off the clear brandy through a thin plastic tube to avoid disturbing the sediment until ca. 50 mL of brandy and sediment was left in the bottle. In order to collect enough sediment, several bottles were syphoned at the same time. The brandy/sediment samples from different bottles were combined, centrifuged, washed with ethanol/water (36% vol.) and dried in an oven at 60 °C.

2.3. Sediment reproduction at laboratory scale

With the aim of reproducing the formation of the sediment in the laboratory, an extract of diatomite was prepared with a suspension of 100 g/L of calcined diatomite similar to that used in brandy filtration in a mixture ethanol/water (36% vol.). Ethanol (96% PA-ACS) and Milli-Q osmosis water were used in this experiment. This suspension was stirred (magnetic stirrer) for 1 h and then centrifuged to obtain a clear extract, which was added to brandy in different concentrations. The samples were analysed for Si at this point and then stored at ambient temperature for 1 month. After this time, Si was analysed again, the amount of sediment was noted and the sediment was separated as described in Section 2.2.

2.4. IR analysis

The sediment was suspended in chloroform and placed drop by drop on a dry KBr window whilst removing the solvent with a stream of hot, dry air. In order to minimise moisture interference, IR spectra of the empty window were recorded before and after measurements and these were digitally subtracted from the sample spectrum. IR spectra were recorded by Fourier Transform Infrared Spectrophotometry (FTIR) using a FTIR-8400S system from Shimadzu (4 cm^{-1} resolution) in the region from 4000 to 400 cm^{-1}.

2.5. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopic (EDX) analysis

Brandy sediment was characterised by SEM and EDX techniques using a Quanta 2000 microscope with a 30 kV acceleration voltage. Prior to analysis the samples were gold- or chromium-coated on carbon tape with a sputtering device by applying 15 mA during 100 s.

2.6. Si and Ca analysis

Si and Ca were analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) without sample treatment using an Iris Intrepid system from Thermo Elemental.

3. Results and discussion

3.1. The appearance of sediment

Sediment formation seems to be related to temperature because it usually appears during winter or at low temperatures with brandy bottled in summer. The sediment is soft and light and its appearance can vary; it can appear as small cotton masses or as a fine dust settled in the bottom of the bottle. Hence, the sediment easily lifts when the bottle is moved or agitated and it takes a long time to settle again (Image 1).

3.2. IR analysis

The FTIR spectrum is shown in Fig. 1 and well-defined absorption bands can be observed. The two bands centred at ca. 450 and 800 cm^{-1} are related to Si–O bond vibrations (Kirk, 1998). The two bands centred at ca. 1080–1160 cm^{-1} are assigned to Si–O–Si in plane vibration (asymmetric stretching) (Wen-Tien, Chi-Wei, & Kuo-Jong, 2006). A band can also be seen at ca. 760 cm^{-1} and this is also characteristic of silica. The symmetric stretching vibrations of Si–O–Si appear at 800 cm^{-1}. The band at 1650 cm^{-1} is due to the bending vibration mode of absorbed water (Fatoni, Koesnarpadi, & Hidayati, 2010). The sharp bands at 1460, 1380, 2930 and 2860 cm^{-1} are assigned to C–H stretch, scissoring

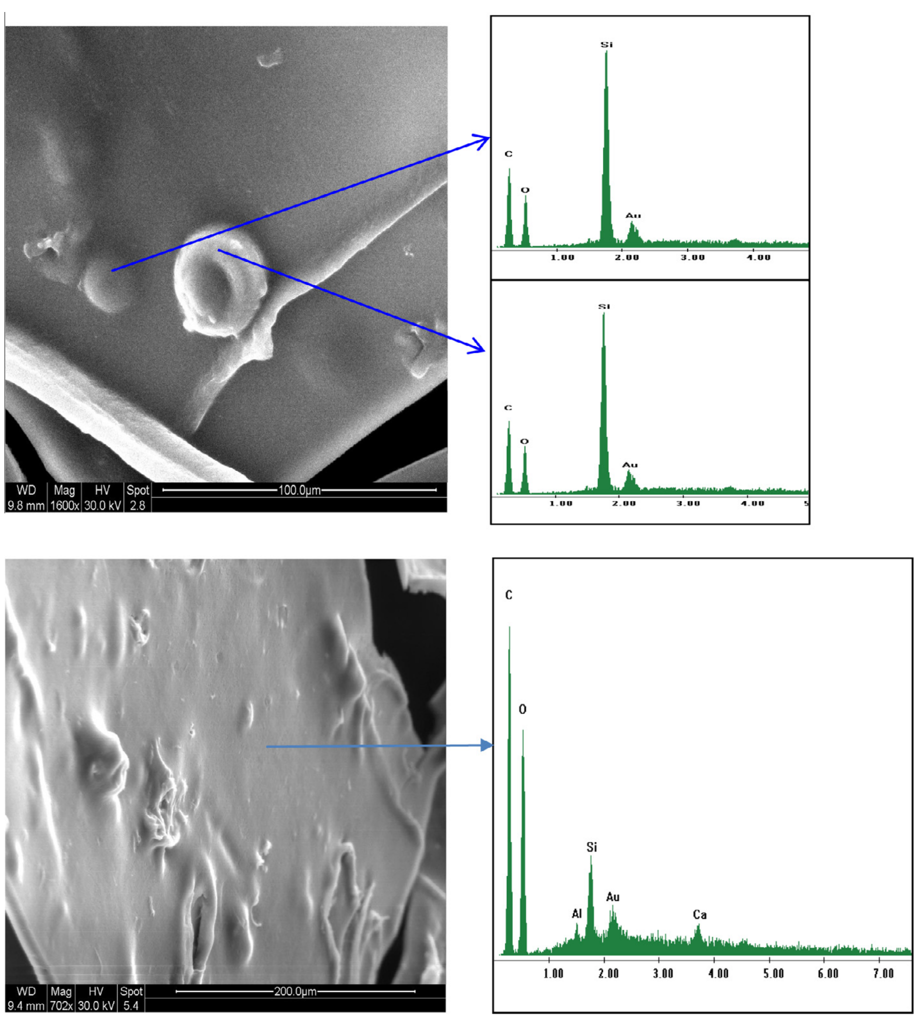

Image 2. SEM and EDX of sediment (real).

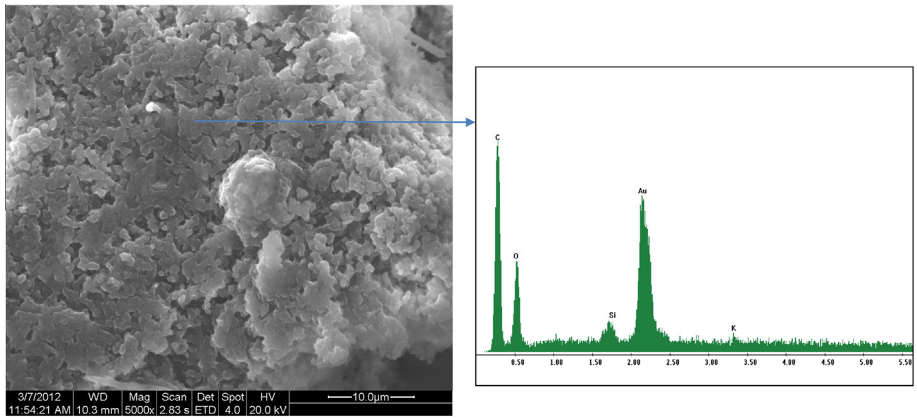

Image 3. SEM micrograph of sediment.

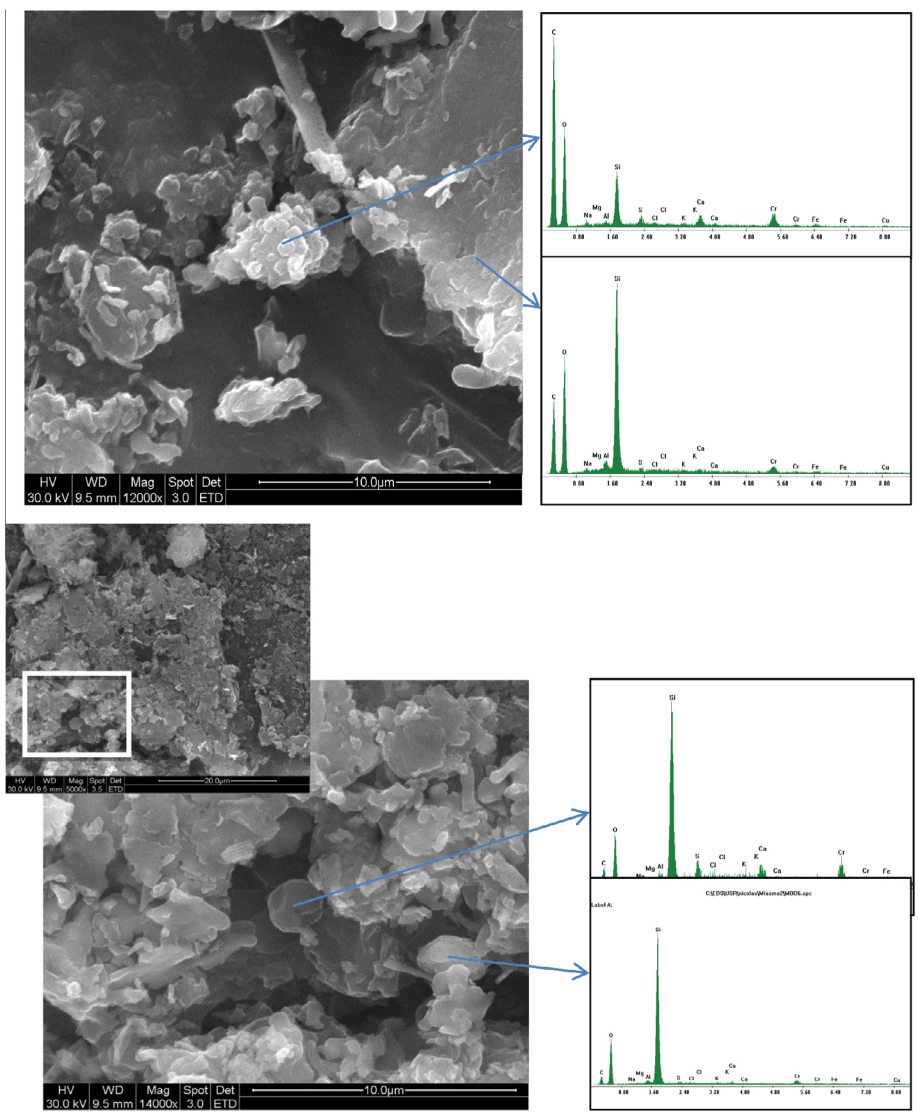

Image 4. SEM and EDX of induced sediment.

and methyl rock bands. Finally, the broad band at 3450 cm^{-1} is due to the overlap of the O–H stretching bands of hydrogen-bonded water molecules and SiO–H stretching of surface silanols hydrogen-bonded to molecular water (Brinker & Scherer, 1990). The observations outlined above confirm the presence of silica and silica-derived compounds in the sediment.

Table 1
Si analysis and sediment formation in brandy added with diatomite extract.

Time	Brandy	Diatomite Extract	Brandy with diatomite extract. Volume added (mL/L)										
			1	2	5	10	15	20	25	30	40	50	100
	Si (μg/L)												
Initial	189	20,527	191	210	251	331	416	528	584	683	816	992	1811
After 1 month	189	20,527	191	205	246	321	400	460	505	558	645	772	1363
Amount of sediment[a]	– – –	– – –	– – –	– – –	– – –	+	+	++	++	+++	+++	+++	+++

[a] – – –: Without sediment; +: very light sediment; ++: medium sediment; +++: heavy sediment.

3.3. SEM micrograph and EDX analysis of sediment

Natural sediment in brandy is mainly formed by silica particles covered by organic residues, as can be observed in Image 2. The top image shows two particles with similar composition and a high Si/C–O ratio, as determined by EDX spectroscopy. These particles seem to be covered by some organic matter. In contrast, the sediment shown in the bottom image is formed by organic matter and silica with a low Si/C–O ratio and there is evidence of some other chemical elements as background in the spectrum, which come from the filtration process (Ca, Al and others). Au originates from the gold coating treatment used on the tape. An enlarged view is shown in Image 3 of the sediment with a particulate structure and low ratio Si/C–O similar to that of Image 2 (bottom).

The process reproduced in the laboratory leads to induced sediments with similar characteristics to the real sediment, as can be seen from Image 4. In the top image, the central cluster is mainly organic matter and residues covered by some silica and this has a low ratio Si/C–O. The crust on the right is high in silica with some remaining organics and a high ratio Si/C–O. This seems to be a fragment of a larger particle. On the other hand, the lower image shows the formation, in this induced process, of small particles of silica with a size of 2 μm and this is the result of the re-precipitation of the added silica, thus corroborating the assumption that sediment in brandy comes from silica released from the diatomite. Evidence for Cr in the EDX spectra of the sample shown in Image 4 is due to the chromium coating treatment used in this case.

3.4. Si analysis and formation of sediment in the laboratory

The results of the Si analysis of brandy with added diatomite extracts are very interesting, as can observed from the values in Table 1. Firstly, the diatomite extract shows a high concentration of silica, which confirms the solubility of silica in diatomite (Gómez et al., 2014). The addition of extract to brandy increases the initial concentration at a rate that is directly related to the volume added. After 1 month, the concentration of silica in the extract remained constant but it had decreased in all samples by an extent that was directly related to the Si concentration. This finding confirms that dissolved silica is not stable in brandy for prolonged periods and that it reacts with some component of the brandy, as stated by Iler (1979). At the same time, sediment appeared in the bottom of the bottle and the amount was directly related to the decrease in the concentration of silica.

4. Conclusions

The sediment found in some bottles of brandy mainly consists of silica along with organic matter. Moreover, silica originating from diatomite is not stable in brandy and when it is added to brandy its concentration decreases after 1 month to an extent that is directly related to the amount initially added. A siliceous sediment appeared at the bottom of the bottle and this had a similar composition to the sediment found in unstable brandy. The amount of sediment is directly related to the decrease in silica concentration. As a final conclusion, it can be stated that the sediment that appears in bottles of brandy is formed from silica released during diatomite brandy filtration.

References

Bauer, K. H., Hinkel, S., Neeb, R., Eichler, P., & Eschnauer, H. R. (1995). Silicon in wine. A trace element – Vinogramme. *Wein-Wissenschaft, 50*(4), 118–122.

Bergner, K. G., & Braun, G. (1984). Studies of the chromium contents of wines. Part 3: Influencing the chromium content of must and wine through technological measures. *Mitteilungen Klosterneuburg, 34*(2), 73–80.

Brinker, C. J., & Scherer, G. W. (1990). *Sol–gel science. The physics and chemistry of sol–gel processing*. New York: Academic Press, pp 581–585.

European-Union (2008). Regulation (EC) 110/2008 of the European Parliament and of the Council on the definition, description, presentation, labelling and the protection of geographical indications of spirit drinks and repealing Council Regulation (EEC) No 1576/89. *Official Journal of the European Union, L 39*, 16–54.

Fatoni, A., Koesnarpadi, S., & Hidayati, N. (2010). Synthesis, characterization and application of diatomaceous earth – 4,4-diaminophenylether-O-hydroxybenzaldehyde as an adsorbent of Ag(I) metal ion. *Indonesian Journal of Chemistry, 10*(3), 315–319.

Gómez, J., Gil, A., De la Rosa-Fox, N., & Alguacil, M. (2014). Diatomite releases silica during spirit filtration. *Food Chemistry, 159*, 381–387.

Gómez-Benítez, J. (1992). Stability of Jerez Brandy. *Vitivinicultura, 2*, 46–50.

Hamrouni, B., & Dhahbi, M. (1999). La silice dans le traitement des eaux. Aspects analytques et procédés d'élimination. *Journal de la Société Chimique de Tunisie, IV*(6), 461–474.

Iler, R. K. (1979). *The chemistry of silica*. New York.

Interesse, F. S., Lamparelli, F., & Alloggio, V. (1984). Mineral contents of some southern Italian wines. I. Determination of boron, aluminum, silicon, titanium, vanadium, chromium, manganese, iron, nickel, copper, zinc, molybdenum, tin, lead by inductively coupled plasma atomic emission spectrometry (ICP-AES). *Zeitschrift fuer Lebensmittel-Untersuchung und-Forschung, 178*(4), 272–278.

Junta-de-Andalucia (2005). Order of June 13 2005 approving the regulation of the specific appellation "Brandy de Jerez" and its regulatory council. *BOJA, 122*, 38–45.

Kirk, C. T. (1998). Quantitative analysis of the effect of disorder-induced mode coupling on infrared absorption in silica. *Physical Review B, 38*(2), 1255–1273.

Martin, K. R. (2007). The chemistry of silica and its potential health benefits. *The Journal of Nutrition, Health and Aging, 11*(2), 94–98.

Ministry of the Presidency, Spain (2014). Royal Decree 164/2014, of March 14, by laying down additional rules for the production, description, presentation and labelling of certain spirits. *Official Bulletin of the State, 74*(I), 26570–26577.

Mohamedbakr, H., & Burkitbaev, M. (2009). Elaboration and characterization of natural diatomite in Aktyubinsk/Kazakhstan. *Open Mineralogy Journal, 3*, 12–16.

OIV. (2002). Resolution Oeno 10/2002. Diatomite. In International Organisation of Vine and Wine (OIV) (Ed.), *International oenological codex*. Paris.

Powell, J. J., McNaughton, S. A., Jugdaohsingh, R., Anderson, S. H. C., Dear, J., Khot, F., et al. (2005). A provisional database for the silicon content of foods in the United Kingdom. *British Journal of Nutrition, 94*, 804–812.

Schwarz, M., Rodriguez, M. C., Guillen, D. A., & García, C. (2011). Analytical characterisation of a Brandy de Jerez during its ageing. *European Food Research and Technology, 232*(5), 813–819.

Stockley, C. S., Smith, L. H., Tiller, K. G., Gulson, B. L., Osborn, C. D. A., & Lee, T. H. (2003). Lead in wine: A case study on two varieties at two wineries in South Australia. *Australian Journal of Grape and Wine Research, 9*(1), 47–55.

Sulpizio, T. E. (1999). Advances in filter aid and precoat filtration technology. In A. F. S. Society (Ed.), *Annual technical conference*, (pp. 1–16). Boston, Massachusetts.

Theune, C., & Bellet, J. (1988). Aptitude of diatomaceous ore for filter aid processing. In 8° *Ind. Min. Conference*, (pp. 223–229).

Wang, L. K. (2006). Diatomaceous earth precoat filtration. In *Handbook of environmental engineering*, (pp. 155–189).

Warwicker, L. A. (1960). Instability in potable spirits. I. Scotch whisky. *Journal of the Science of Food and Agriculture, 11*, 709–716.
Warwicker, L. A. (1963). Instability in potable spirits. II. Rum and brandy. *Journal of the Science of Food and Agriculture, 14*, 365–371.
Wen-Tien, T., Chi-Wei, L., & Kuo-Jong, H. (2006). Characterization and adsorption properties of diatomaceous earth modified by hydrofluoric acid etching. *Journal of Colloid and Interface Science, 297*, 749–754.